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We are pleased to report extensive progress in a number of areas in thermodynamics, kinetics, and stochastic theories in non-linear chemical reactions far from equilibrium. Research includes both theoretical and experimental studies. Specific areas of research include the following: 1. Thermodynamic and Stochastic Theory of Electrical Circuits; 2. Thermodynamic and Stochastic Theory for Non-equilibrium Systems with Multiple Reactive Intermediates: The Comcept and Role of Excess Work; 3. The relation of Fluxes and forces to work in Nonequilibrium Systems; 4. Multiple Steady States in Coupled Flow Tank Reactors; 5. Thermodynamic and Stochastic Theory for Non-ideal Systems Far from Equilibrium; 6. Thermodynamic and Stochastic Theory of Reaction Diffusion Systems with Multiple Stationary States; 7. Stationary Probability Distribution Near Stable Limit Cycles Far from Hopf Bifurcation Points; 8. Fluctuation-dissipation Relations for Chemical Systems; 9. Thermodynamic and Stochastic Theory of Nonequilibrium systems: Fluctuation Probabilities and excess Work; 10. Thermodynamic and Stochastic Theory of Non-equilibrium Systems: A Lagrangian Approach to Fluctuations and Relation to excess work. Experiments on Relative Stability in the Bistable Multivariable

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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

THEORY AND EXPERIMENTS ON CHEMICAL INSTABILITIES

by

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For the Period: April 1991 to December 1994.

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I. Research Accomplishments for the period April 1991 to December 1994.

We are pleased to report extensive progress in a number of areas in thermodynamics, kinetics, and stochastic theories in non-linear chemical reactions far from equilibrium. Research includes both theoretical and experimental studies. The numbers in parenthesis refer to the principle investigator's publication list which is appended to this report. The starred items on the publication list acknowledge the sponsorship of that research by the Air Force Office of Scientific Research.

A. Theory and Experimentation on the Thermodynamics of Systems Far from Equilibrium

1. Thermodynamic and Stochastic Theory of Electrical Circuits

We have made a development of a thermodynamic and stochastic theory of electrical circuits approaching nonequilibrium stationary states containing linear or nonlinear capacitors, resistors, and inductors. We restrict ourselves to circuits with only point attractors. The theory centers around a function υ and we show that (1) it is the macroscopic driving force to a stationary state, (2) it is a global Liapunov function, (3) it provides necessary and sufficient conditions for the existence and stability of stationary states, (4), its time derivative is a component of the total dissipation, (5) it is an excess work of moving the circuit away from the stationary state, and (6) it determines

a stationary probability distribution of a Fokker-Planck equation. The generalization from linear to nonlinear circuits is made with the concept of an instantaneous mapping from the nonlinear circuit to a thermodynamically and kinetically equivalent linear circuit. A translation of chemical to electrical networks holds at the thermodynamic but not stochastic level of description. This work is natural extension of prior studies on chemical systems to electrical circuits. The work has been published in Phys. Rev. A (278).

2. Thermodynamic and Stochastic Theory for Nonequilibrium Systems with Multiple Reactive Intermediates: The Concept and Role of Excess Work

We continue our development of a global thermodynamic and stochastic theory of open chemical systems far from equilibrium with an analysis of a broad class of isothermal, multicomponent reaction with multiple steady states, studied under the assumption of local equilibrium. We generalize species-specific affinities of reaction intermediates, obtained in prior work for nonautocatalytic reaction mechanisms, to autocatalytic kinetics and define with these affinities an excess free energy differential $\delta\phi$. The quantity $\delta\phi$ is the difference between the work required to reverse a spontaneous concentration change and the work available when the same concentration change is imposed on a system in a reference steady state. The integral of $\delta\phi$ is in general not a state function; in contrast, the function ϕ_{det} obtained by

integrating $\delta\phi$ along deterministic kinetic trajectories is a state function, as well as an identifiable term in the time-integrated dissipation. Unlike the total integrated dissipation ϕ_{det} remains finite during the infinite duration of the system's relaxation to a steady state and hence ϕ_{det} can be used to characterize that process. The variational relation $\delta\phi \geq 0$ is shown to be a necessary and sufficient thermodynamic criterion for a stable steady state in terms of the excess work of displacement of the intermediates and ϕ_{det} is a Liapunov function in the domain of attraction of such steady states. Based on these results and earlier work with nonautocatalytic and equilibrating systems, we hypothesize that the stationary distribution of the master equation may be obtained in the form $P_S = N \exp(-\phi_{det}/kT)$ and provide an analytical argument for this form for macroscopic systems. This generalizes the Einstein fluctuation formula to multivariable systems with multiple steady states, far from equilibrium. This work has been published in J. Chem. Phys. (279).

In a separate article we tested the extension to systems with multiple components and multiple stationary states by numerical solutions of the master equation for such systems. We found agreement for two separate models and showed that the excess work is a solution of the master equation thus in analogy to equilibrium thermodynamics the excess work provides the probability of a fluctuation from a stationary state and provides the macroscopic driving force for the

deterministic kinetics back to the stationary state. This work has been published in the J. of Chem. Phys. (280).

3. The Relation of Fluxes and Forces to Work in Nonequilibrium Systems

Prior work has shown that an excess work is necessary to displace a chemical or physical system from a stationary state, and this excess work determines the stationary distribution of a stochastic birth-death master equation. We derive the augmentation of this master equation for a one-variable system in the presence of external noise. When this noise is much larger than internal noise, but still small compared to macroscopic averages, then the stationary distribution reduces to a form suggested by Landau and Schlögl, which is the integral of the flux of the deterministic kinetic equation. A similar result was obtained on the basis of an assumed Fokker-Planck equation. Hence, in the presence of external forces exceeding in intensity the internal fluctuations, fluxes are proportional to forces without linearization in concentrations. This work has been published in the J. Chem. Phys. (271).

4. Multiple Steady States in Coupled Flow Tank Reactors

Coupling between continuous-flow, stirred tank reactors (CSTR's), each having multiple steady states, can produce new steady states with different concentrations of the chemical species in each of the coupled tanks. In this work, we identify a kinetic potential ψ that governs the deterministic

time evolution of coupled tank reactors, when the reaction mechanism permits a single-variable description of the states of the individual tanks; examples include the iodate-arsenous acid reaction, a cubic model suggested by Noyes, and two quintic models. Stable steady states correspond to minima of ψ, and unstable steady states to maxima or saddle points; marginally stable states typically correspond to saddle-node points. We illustrate the variation in ψ due to changes in the rate constant for external material intake (k_o) and for exchange between tanks (k_x). For fixed k_o values, we analyze the changes in numbers and types of steady states as k_x increases from zero. We show that steady states disappear by pairwise coalescence; we also show that new steady states may appear with increasing k_x, when the reaction mechanism is sufficiently complex. For fixed initial conditions, the steady state ultimately reached in a mixing experiment may depend on the exchange rate constant as a function of time, $k_x(t)$: Adiabatic mixing is obtained in the limit of slow changes in $k_x(t)$ and instantaneous mixing in the limit as $k_x(t) \to \infty$ while t remains small. Analyses based on the potential ψ predict the outcome of mixing experiments for arbitrary $k_x(t)$. We show by explicit counterexamples that a prior theory developed by Noyes does not correctly predict the instability points or the transitions between steady states of coupled tanks, to be expected in mixing experiments. We further show that the outcome of such experiments is not connected to the relative stability of

steady states in individual tank reactors. We find that coupling may effectively stabilize the tanks. We provide examples in which coupled CSTR's can be operated stably with one of the tanks at or beyond the single-tank marginal stability point. This work has been published in the J. Chem. Phys. (284).

5. Thermodynamic and Stochastic Theory for Non-ideal Systems Far from Equilibrium

The thermodynamic and stochastic theory of nonlinear chemical kinetics systems, possibly with multiple stable stationary states, is extended to non-ideal species, either nonlinear gases or nonlinear solutions. The Bronsted theory of the kinetics of non-ideal species is chosen for explicit formulation of this extension, but the development is similar for other choices. This work has been published in the J. of Chem. Phys. (299).

6. Thermodynamic and Stochastic Theory of Reaction Diffusion Systems with Multiple Stationary States

The thermodynamic and stochastic theory of chemical systems far from equilibrium is extended to reactions in inhomogeneous systems for both single and multiple intermediates, with multiple stationary states coupled with linear diffusion. The theory is applied to the two variable Sel'kov model coupled with diffusion, in particular to the issue of relative stability of two stable homogeneous stationary states as tested in a possible inhomogeneous experimental configuration. The thermodynamic theory

predicts equistability of such states when the excess work from one stationary state to the stable inhomogeneous concentration profile equals the excess work from the other stable stationary state. The predictions of the theory on the conditions for relative stability are consistent with solutions of the deterministic reaction-diffusion equations. We apply the theory again to the issue of relative stability for single-variable systems, and make comparison with numerical solutions of the reaction-diffusion equations for the Schlögl model, and with experiments on an optically bistable system where the kinetic variable is temperature and the transport mechanism is thermal conduction. This work has been accepted for publication in the J. of Chem Phys. 1993 (304).

7. Stationary Probability Distribution Near Stable Limit Cycles Far from Hopf Bifurcation Points

We obtain analytic results for the stationary probability distribution in the vicinity of a stable limit cycle for Markov systems described by a Fokker-Planck equation or a birth-death master equation. The results apply best for ranges of parameters removed from Hopf bifurcation points. As a by-product, we demonstrate that there holds a Liouville-like theorem for the stationary probability distribution: the product of the velocity along the limit cycle times the area of the cross section of the probability distribution transverse to the cycle is a constant. A numerical simulation of a chemical model system with a limit

cycle shows good agreement with the analytic results. This work has been published in Physical Review E (306).

8. Fluctuation-dissipation Relations for Chemical Systems

A new fluctuation-dissipation relation is suggested for constant step, one intermediate chemical processes far from equilibrium. It establishes a relationship between the net reaction rate $\tilde{t}(x)$, the probability diffusion coefficient $D(x)$ in the composition space and the species-specific affinity $A(x)$: $\tilde{t}(x) = 2D(x)$ tangh $(-A(x)/2kT)$, where X is the concentration of the active intermediate, k is Boltzmann's constant and T is the absolute temperature. The theory is valid for nonlinear fluctuations of arbitrary size. For macroscopic systems the fluctuation-dissipation relation may be viewed as a force-flux relationship. We distinguish four fluctuation-dissipation regimes which correspond to the decrease of the absolute value of the species-specific affinity. The passage from high $|A(x)|$ to small $|A(x)|$ corresponds to a crossover from a linear dependence of the species-specific dissipation rate $\dot{\phi}(x)$ on $|A(x)|$, $\dot{\phi}(x) \sim -|A(x)|$, to a square one $\dot{\phi}(x) \sim -A^2(x)$. A main feature of the fluctuation-dissipation relation is its symmetry with respect to the contributions of the forward and backward chemical processes to fluctuation and relaxation. Two new physical interpretations of the probability diffusion coefficient are given: one corresponds to a measure of the strength of fluctuations at a steady state, and the other to a measure of the instability of a given fluctuation state.

The dispersion of the number q of reaction events in a given time interval is given by a generalized Einstein relation $\langle \Delta q^2 \rangle = 2VD(x)t$, where V is the volume of the system. The diffusion coefficient $D(x)$ is proportional to the reciprocal value of the mean age $\langle \tau(x) \rangle$ of a fluctuation state characterized by the concentration X: $D(x) = 1/(2V\langle \tau(x) \rangle)$. These interpretations are not related to the use of a Fokker-Planck approximation of the chemical master equation. This work has been published in the Journal of Chemical Physics (314).

9. Thermodynamic and Stochastic Theory of Nonequilibrium systems: Fluctuation Probabilities and Excess Work.

For a nonequilibrium system described at the mesoscopic level by the master equation, we prove that the probability of fluctuations about a steady state is governed by a thermodynamic function, the "excess work." The theory applies to systems with one or more nonequilibrium steady states, for reactions in a compartment that contains intermediates X_j of variable concentration, along with a reactant A and product B whose concentrations are held constant by connection of the reaction chamber to external reservoirs. We use a known relation between the stationary solution $P_s(X)$ of the master equation and an underlying stochastic Hamiltonian H: to logarithmic accuracy, the potential that gives $P_s(X)$ is the stochastic action S evaluated along fluctuational trajectories, obtained by solving Hamilton's equations of motion starting at a steady state. We prove that the

differential action dS equals a differential excess work $d\phi^\circ$, and show that $d\phi^\circ$ can be measured experimentally in terms of total free energy changes for the reaction compartment *and* the reservoirs. Thus we connect the probability of concentration fluctuations in an open reaction compartment to thermodynamic functions for the entire closed system containing the compartment. The excess work $d\phi^\circ$ is the difference between the total free energy change for a specified change in the quantities of A, X, Y, and B in the state of interest, and the free energy change for the same changes in species numbers, imposed on the same system in a reference state (A, X°, Y°, B). The reference-state concentration for species X_j is derived from the momentum p_j canonically conjugate to X_j along the fluctuational trajectory. For systems with linear rate laws, the reference state (A, X°, Y°, B) is the steady state, and ϕ° is equivalent to the deterministic excess work ϕ^*_{det} introduced in our previous work. For nonlinear systems, (A, X°, Y°, B) differs from the deterministic reference state (A, X*, Y*, B) in general, and $\phi^\circ \neq \phi^*_{det}$. If the species numbers change by ±1 or 0 in each elementary step and if the overall reaction is a conversion $A \rightarrow X \rightarrow Y \rightarrow B$, the reference state (A, X°, Y°, B) is the steady state of a corresponding linear system, identified in this work. In each case, $d\phi^\circ$ is an exact differential. Along the fluctuational trajectory away from the steady state, $d\phi^o > 0$. Along the deterministic kinetic trajectory, $d\phi^\circ \leq 0$, and ϕ° is a Liapunov function. For two-variable systems

linearized about a steady state, we establish a separate analytic relation between Ps(X), ϕ^*det, and a scaled temperature T*. This work has been accepted for publication in the Journal of Chemical Physics (321).

10. Thermodynamic and Stochastic Theory of Non-equilibrium Systems: A Lagrangian Approach to Fluctuations and Relation to Excess Work

The dynamics of fluctuations in systems approaching a non-equilibrium steady state, with or without detailed balance, are investigated by means of Lagrangian function, which is derived from the generator of time displacement (Hamiltonian) of the mesoscopic evolution equation. In the thermodynamic limit, the stationary probability distribution for the fluctuating variables is expressed in terms of the action of this stochastic Lagrangian along the fluctuational trajectory, the most probable path of infinite duration for the generation of a particular fluctuation away from the steady state. The fluctuational trajectory is related by a gauge-like transformation to the deterministic trajectory, which is the most probable path for the relaxation of the macroscopic system to the steady state. This framework is applied to the analysis of one-variable chemical reactions modeled by a constant step master equation, and to two-variable systems in the linearized region around the steady state, where the fluctuations are described by a linear Fokker-Planck equation. In these examples, the thermodynamic significance of the action along the fluctuational trajectory

is established by relating the irreversible (odd under time inversion) part of the Lagrangian and the time derivative of a deterministic excess work. This work has been accepted for publication in the Journal of Chemical Physics (322).

B. Experiments on Chemical and Physical Instabilities

1. Experiments on Relative Stability in the Bistable Multivariable Bromate-Ferroin Reaction

We report the first measurements of the relative stability of two stable stationary states in a multivariable chemical system, the bromate-ferroin reaction. The two stable stationary states are established in two CSTR under the same constraints and then brought in contact in a laminar flow reactor with a sharp boundary between the two stationary states. The flow through the laminar reactor is then stopped and the boundary propagates into the less stable of the two stable stationary states. We measure the velocity of front propagation; extrapolation to zero velocity determines conditions of equistability of the two stationary states. The article provides substantial experimental corroboration for our thermodynamic theory of irreversible processes far from equilibrium. This work has been published in the J. Phys. Chem. (302).

2. Observations of Pattern Evolution in Thermal Convection

High-resolution measurements of the mean temperature gradient field of a fluid undergoing thermal convection in a vertical slot were made. The detection method employs

schlieren optics with a linear photo diode array detector. With proper calibration the schlieren signals permit quantitative reconstruction of the varying temperature field along one dimension in the fluid, with a relative temperature resolution of ± 0.02 K. The critical applied temperature difference, $\Delta T_{b,c}$, is determined by extrapolation of the measured convection pattern amplitudes. The measurements permit detailed monitoring of the wave number distribution and its development in time as well as harmonic analysis of the temperature waveform. The stability limits of convective patterns are investigated as a function of forcing and wave number and the observed limits are compared to theoretical predictions. The details of the transitions from conduction to convection and from one convective spatial pattern to another are observed and analyzed as the degree of forcing is varied. The creation and destruction of convective roll cells is observed as is the propagation of convective flow across the slot. This work has been published in the J. of Phys. Fluids A (272).

3. Critical Slowing Down in Optically Bistable Systems

We measure relaxation rates near the critical point and the left hysteresis limit of an optically bistable system, ZnSe interference filter. Our ZnSe system has an inhomogeneous geometry where a long, narrow illuminated region has boundaries at a temperature near and below that of the lower state. We determine the critical angle, the angle

of incidence of light at which the hysteresis limits coalesce to form a critical point, and perturb the system by changing the input power beyond the critical point. For incidence angles equal to or slightly greater than the critical angle, we find that relaxation rates increase exponentially as the critical point is approached. The critical exponents for perturbations which increase the input power beyond the critical point are greater than those for perturbations which decrease the input power. In either case, the critical exponents increase as the angle of incidence approaches the critical angle. When the hysteresis region is large, we find slowing down near the left hysteresis limit in accordance with our calculations based on a one-dimensional inhomogeneous model. This work has been published in the J. Chem Phys. (282).

4. Experimental Stabilization of Unstable Steady States in Oscillatory and Excitable Reaction Systems

A feedback method is used to stabilize unstable stationary states in experiments with the chlorite-iodide reaction. The unstable stationary states occur in oscillatory and excitable regions of constraint space. Stabilization of unstable steady states provides information about these states and may be of practical importance. An analytical study of a model mechanism of this reaction is consistent with the experiments. This feedback method does not create new stationary states but stabilizes unstable stationary states present in the autonomous system. Unlike

"thermostat" type methods, knowledge of the exact location of the unstable stationary states of the autonomous system is not required to implement this feedback method. This work has been published in the Journal of Physical Chemistry (308).

5. Stabilization of Unstable Spatial Structures in an Optically Bistable System

We stabilize the unstable steady state of a spatially inhomogeneous optically bistable ZnSe interference filter and measure the average intensity of the light transmitted and reflected by the filter. We also image the spatial structures which are the stable and unstable steady states by spatially resolving the transmitted light. We further measure relaxations from the unstable branch to the two stable branches. Relaxations to the low-temperature branch occur homogeneously while relaxations to the high-temperature branch occur by the propagation of a front. The results are in agreement with calculated predictions of a deterministic model of this system. A comparison is also made to nonlinear reaction-diffusion systems. This work has been published in the Journal of Physical Chemistry (309).

C. Experiments on Chemical Waves

1. Profiles of Chemical Waves

We report measurements and numerical calculations of profiles of chemical waves in the ferroin-catalyzed Belousov-Zhabotinskii (BZ) reaction at various concentrations of reactants and study waves traveling in an excitatory as well

as an oscillatory medium. The fronts of the waves in the excitatory medium are generally broader and somewhat bent, while the fronts of waves in the oscillatory mediums are narrower and straighter. In both cases, the measured concentration of ferroin, which defines the structure of the wave increases with increasing initial concentration of sulfuric acid and sodium bromate and decreases with increasing initial concentration of malonic acid. We model the waves by modifying the existing extended Oregonator model, and the concentrations of ferroin of the numerically calculated wave profiles agree better with measurements than those of previous models. This work has been published in the J. of Phys. Chem. (275).

2. Origin of Spontaneous Wave Generation in Excitable Chemical Systems

We investigate the origin of spontaneous chemical wave generation in an excitable Belousov-Zhabotinskii system. We solve one-dimensional reaction-diffusion equations of an Oregonator model with the initial profiles possessing an excitation of varying concentration of either $HBrO_2$ or Br^-, and the excitation occurs within a region of different length. The concentration of the threshold excitation necessary for a wave to propagate depends on the length within which the initial excitation is applied. We further perform an equilibrium stochastic calculation of the recurrence time for a thermal fluctuation to induce a change in concentration of a sufficient magnitude within a

sufficient volume for a wave to propagate. The smallest recurrence time calculated is 10^{17}s. We compare our results with previous experiments and calculations and conclude from all the evidence that an internal thermal fluctuation is highly unlikely to generate a chemical wave in an excitable chemical solution. This work has been published in the J. of Phys. Chem. (290).

3. Origin of Spontaneous Wave Generation in an Oscillatory Chemical System

The origin of spontaneously generated chemical waves in an oscillatory Belousov-Zhabotinskii reaction has been investigated by numerical calculations of the deterministic reaction-diffusion equations of a modified Oregonator model and by equilibrium stochastic calculations. From numerical calculations, we obtain threshold perturbations in the phase of oscillations and in the concentrations of $HBrO_2$ and Br^- within areas of space with varying radii necessary to initiate trigger waves. Inward propagating trigger waves initiated by a phase shift in the perturbed region with respect to the bulk solution have been observed in the calculations for the first time. Perturbations smaller than the threshold perturbations or in regions with smaller radii lead to phase-diffusion waves. Our equilibrium stochastic calculations show that the recurrence time for a thermal fluctuation to induce a change in the $HBrO_2$ concentration of sufficient magnitude within a sufficient volume for a trigger wave to propagate is many orders of magnitude larger than the

observation of time of traveling wave experiments. We concluded that an internal thermal fluctuation is highly unlikely to generate a trigger wave in an oscillatory chemical solution. This work has been published in the J. of Phys. Chem. (292).

4. Propagating and Stationary Patterns in Reaction-Transport Systems: Generic Mechanisms, Spatial Geometries and Response to External Fields

The variety of origins, structures and occurrences of non-linear waves in reaction-transport systems is reviewed. Generic mechanisms of wave and pattern development are shown to be closely associated with underlying mathematical structure such as multiplicity in steady-state behavior, chemical oscillations, small-amplitude instabilities, and inherent degeneracies such as occurs when several species behave similarly chemically. Cellular automata and adaptive gridding approaches to the analysis of waves and other patterns are contrasted. The types of phenomena that can occur in two and three spatial dimensions are noted to be spirals and rotors and static, periodic and aperiodic knotted structures.

The electrical response and autonomous behavior of electrolyte systems is reviewed, as are applications in biological and geological systems. This work has been published in Advances in Porous Media, Vol. 2, Chapter 2, pages 107-143, edited by M. Yavuz Corapcioglu (Elsevier, 1994). (295).

D. Towards a Strategy of Determining Reaction Mechanisms

1. Experimental Determination of Bifurcation Features of the Chlorite-iodide Reaction

We present results for experiments suggested by a theoretical study of the Citri-Epstein mechanism for the oscillatory chlorite-iodide reaction. We determine the bifurcation structure of this system on axes of $[ClO_2^-]_0/[I^-]_0$, the ratio of reaction input concentrations, versus log φ_0, the logarithm of the reciprocal residence time, and make a comparison to the theoretical bifurcation structure. The experimental bifurcation structure displays a number of features predicted by theory: an oscillatory region is bounded at high $[ClO_2^-]_0/[I^-]_0$ by a supercritical Hopf bifurcation, and at low $[ClO_2^-]_0/[I^-]_0$ or high log φ_0 by a saddle-node infinite period bifurcation. However, the oscillatory region is somewhat smaller and the excitable region is substantially larger than that predicted by theory. This article has been published in the J. of Phys. Chem. (297).

2. Analysis of a Mechanism of the Chlorite-Iodide Reaction

We present a detailed analysis of the most recent mechanism of the oscillatory chlorite-iodide reaction proposed by Citri and Epstein. First, we use stoichiometric network analysis (SNA) to determine the complete set of major

reaction pathways (extreme currents) of the mechanism under CSTR-conditions. Two qualitatively different types of unstable extreme currents are predicted within the mechanism. At three different steady states the dominant extreme currents (EC) are singled out. Subgroups of elementary reactions ('dynamic elements'), dominant at different times during a cycle of oscillation, are identified. Suggestions for simplifications of the mechanism are given and a simplified oscillatory mechanism is extracted which accounts for the oscillatory behavior of the full mechanism. The SNA-approach constitutes an operational prescription for the analysis of chemical reaction mechanisms, since the major steps of the analysis are based on computational routines. Second, the bifurcation behavior is investigated with particular attention to transitions from non-oscillatory to oscillatory regimes. We calculate one and two-dimensional bifurcations with axes of experimentally convenient constraints. The roles of the chemical species in the mechanism are predicted based on the numerical results of the SNA-analysis. We calculate the phase response of the mechanism as obtained from pulse perturbations of HOCl and ClO_2. This article has been published in the J. Phys. Chem. (298).

3. Towards a Systematic Determination of Complex Reaction Mechanisms

Given a complex chemical reaction with an unknown or a partially known mechanism, we examine the possibility of

determining the essential parts of the mechanism by a number of experimental methods, all of which rely upon the experimental evaluation of the stationary state Jacobian matrix elements (JMEs). If the response by all species to a pulse perturbation of one of the species can be measured, then it is possible to determine all of the JMEs. A different experimental method, a concentration shift experiment, relies on measuring the change of steady state concentrations in a chemical reactor after the inflow of each species has been altered. Another technique employs the induction (or cessation) of oscillations caused by a delayed feedback imposed on an inflow species. If we assume power law kinetics, the connectivity of the reaction network can be determined based on the signs of the JMEs. Once the connectivity of the reaction network has been established, then with some knowledge of basic chemistry, the essential parts of the mechanism can be constructed. Furthermore, the rate coefficients of the suggested reaction rates can be calculated from the measured JMEs. The method of constructing a mechanism is illustrated with JMEs calculated from a model of the horseradish peroxidase reaction. If the inverse of the Jacobian (the concentration shift matrix) or the phase shifts between pairs of oscillating species can be measured, the species in the oscillatory reaction can be classified and the reaction mechanism can be categorized. If, due to experimental constraints, the entire Jacobian cannot be evaluated, these methods offer a new series of

tests that must be passed by an proposed mechanism. Qualitative determination, such as the signs of JMEs, can also be useful. This article has been accepted for publication in the J. Phys. Chem. as a Feature Article (301).

4. New Measurements on the Chlorite-Iodide Reaction and Deduction of Roles of Species and Categorization

We present the results of new experiments on the chlorite-iodide reaction and us these results to determine the roles of various chemical species in the reaction mechanism. We simultaneously monitor three species, I^-, ClO_2^-, and I_2, and determine the relative phases of oscillations in these species. We use perturbations in these species and the additional species NaOCl, IO_3^-, Cl^-, HIO_2, and H_2OI^+ to perform qualitative pulsed-species response, concentration shift regulation, and concentration shift destabilization experiments. Within a scheme of categorization of oscillatory reaction mechanisms, we determine that the chlorite-iodide system is a category 1CX or 1CW oscillator. Further, we distinguish essential and nonessential species, and identify ClO_2^- as a type Z essential species, I^- as a type Y essential species, and HOCl as an essential species of type X or W. HOI and HIO_2 are essential species whose roles we were unable to identify from these measurements. I_2 and IO_3^- are identified as nonessential species of type B, while Cl^- is a nonessential species of type C. Our assignments of the mechanistic roles of the essential species show complete agreement with those

predicted by the Citri-Epstein mechanism. However, that model mechanism predicts that I_2 is a nonessential species of type C and that Cl^- is a nonessential species of type B. This work has been accepted for publication in the Journal of Physical Chemistry (327).